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Electronic structure and exchange interactions of $Na_2V_3O_7$

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We have performed first-principle calculations of the electronic structure and exchange couplings for the nanotube compound $Na_2V_3O_7$ using the local-density approximation Hubbard parameter U approach. Our results show that while the intraring exchange interactions are mainly antiferromagnetic, the inter-ring couplings are *ferromagnetic*. We argue that this is a consequence of the strong hybridization between filled and vacant $3d$ vanadium orbitals due to the low symmetry of $Na_2V_3O_7$, which results into strong, and often dominant, ferromagnetic contributions to the total exchange interaction between vanadium atoms. A comparison with results of previous works is included.

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I. INTRODUCTION

The values of the exchange interactions between the magnetic moments carried by metallic atoms constitute a crucial piece of information for the theoretical investigation of the magnetic properties (magnetization, susceptibility, specific heat, etc.) of low-dimensional quantum $S=1/2$ systems, for instance, vanadates.[1–3] There are several ways to obtain this information. One of them is based on the estimation of the exchange integrals from the hopping parameters obtained by fitting the band structure with an extended tight-binding model[4] or through a downfolding[5] and projection[6] procedure. The first-principle method for the calculation of the exchange interaction parameters was proposed by Lichtenstein *et al.*[7] Within this scheme the exchange interaction parameters are determined by calculating the second variation of the total energy $\delta^2 E$ with respect to small deviations of the magnetic moments from the collinear magnetic configuration.

The earliest theoretical investigations[8,9] of the magnetic couplings of $Na_2V_3O_7$, a Mott insulator with the rather exotic topology of a nanotube, were based on the former method. They relied on different estimates of the hopping integrals and lead to conflicting results. Whangbo and Koo[8] have employed a spin dimer analysis in order to estimate the relative magnitudes of the spin exchange interaction parameters expected for $Na_2V_3O_7$. They have concluded that $Na_2V_3O_7$ could be described by six helical spin chains and should show a gap in the spin excitations.

Dasgupta *et al.*[9] have performed the first *ab initio* microscopic analysis of the electronic and magnetic properties of $Na_2V_3O_7$ using linear augmented plane wave (LAPW) method.[10] They have derived a V $3d$ xy orbital model Hamiltonian using the downfolding procedure within the framework of the Nth order muffin-tin orbital method.[11] The hopping parameters calculated along these lines lead to a picture where the intraring exchange integrals are antiferromagnetic and much larger than the inter-ring ones, a picture supported by the fact that a quantitative fit of the temperature dependence of the susceptibility can be performed assuming decoupled rings.

In this paper we report on a detailed investigation of the isotropic exchange interactions in $Na_2V_3O_7$ based on a first-principle local-density approximation Hubbard parameter U (LDA+U) calculation of its electronic and magnetic structure. The exchange interactions between vanadium atoms were calculated using the Green function method developed by Lichtenstein *et al.*[12] In order to provide a microscopic explanation of the resulting exchange interactions, which are *qualitatively* different from previous estimates, we have used an extended Kugel-Khomskii model that includes the hybridization between filled and vacant orbitals using the hopping parameters calculated by the projection procedure. We conclude that estimating the exchange interactions of a system with a very exotic geometry such as $Na_2V_3O_7$ within simple superexchange between xy orbitals with on-site Coulomb interaction is not possible.

The paper is organized as follows. In Sec. II we shortly describe the crystal structure of $Na_2V_3O_7$ and present the results of the LDA calculation. In Sec. III we present the results of the LDA+U calculation, and we discuss the origin of the exchange interaction parameters. In Sec. IV we briefly summarize our results.

II. LDA CALCULATION

A simplified view of the crystal structure of $Na_2V_3O_7$ is presented in Fig. 1. The main building blocks of the crystal structure are distorted vanadium-oxygen pyramids. Vanadium atoms are roughly in the center of a pyramid which is built by five oxygen atoms. There are three types of vanadium atoms, V1, V2, and V3, which form a basic structure unit. Three of these units connected by edges are needed to form a ring of the tube. The lowest energy orbital is the V $3d$ orbital of xy symmetry[3] (using a convention where the axes of the coordinate system are directed towards the oxygen ions in the plane), which is the orbital whose lobes point away from the oxygen. More detailed information about the crystal structure of $Na_2V_3O_7$ can be found in Ref. 13.

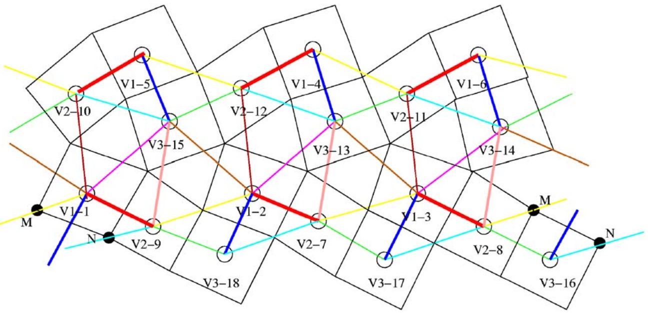

FIG. 1. (Color online) Simplified crystal structure and interaction paths between vanadium atoms in $Na_2V_3O_7$. Equivalent interaction paths have the same color. The tube structure is made by putting M and N into contact.

The electronic structure calculation of $Na_2V_3O_7$ was performed using the tight binding linear-muffin-tin-orbital atomic sphere approximation (TB-LMTO-ASA) method in terms of the conventional local-density approximation.[14] The band structure of $Na_2V_3O_7$ obtained from LDA calculations is presented in Fig. 2. There are 18 bands near the Fermi level which have xy symmetry (since there are 18 vanadium atoms in the unit cell) and are separated from the other V $3d$ bands as well as from the $2p$ oxygen bands. The corresponding partial densities of states are shown in Fig. 3. Six bands have an energy significantly lower than the others, which are located near the Fermi level. Two of them have an energy near −0.7 eV, while the other four are located between −0.3 and −0.4 eV. Such a band location of active orbitals (occupied by electrons) is unusual in comparison with the band structure of other $S=1/2$ transition metal compounds.[15] These bands are in good agreement with those presented in Ref. 9.

With one subset of energy bands well separated from the rest, one can expect that a tight-binding model with a single xy orbital per V site (i.e., a 18-band model) will provide a good approximation to the full band structure close to the Fermi level.

For this we express the LDA band structure results in terms of the low-energy model Hamiltonian

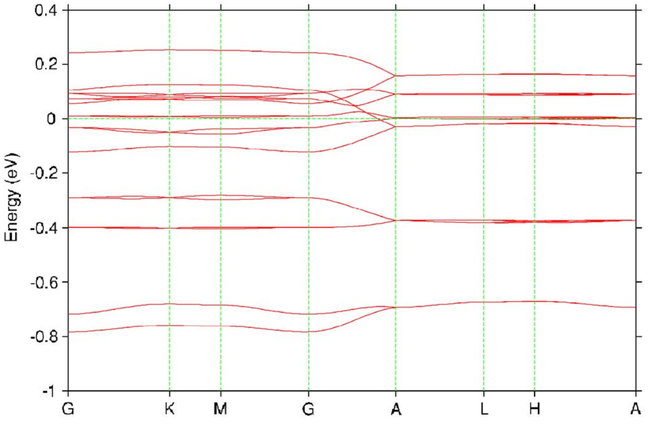

FIG. 2. (Color online) Band structure of $Na_2V_3O_7$ near the Fermi level (0 eV).

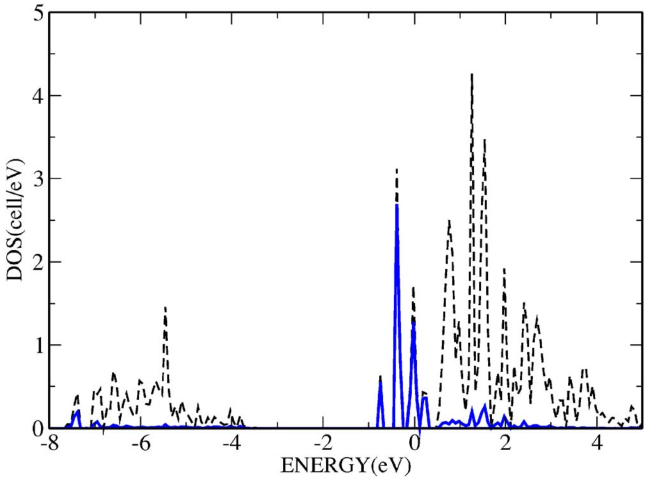

FIG. 3. (Color online) Partial density of $3d$ vanadium states obtained from LDA calculations. The solid blue and the dashed black lines are the density of states of $3d_{xy}$ and the total density of $3d$ states, respectively.

$$H_{TB} = \sum_{i,j,\sigma} t_{ij} a^{+}_{i\sigma} a_{j\sigma}, \tag{1}$$

where i and j are site indexes, t_{ij} is the effective hopping integral between sites i and j, and $a^{+}_{i\sigma}$ is the operator which creates an electron with a spin σ in a state with a Wannier function centered at the ith atom. In order to obtain the hopping parameters t_{ij}, we have employed the projection procedure.[6] According to this procedure, the hopping integrals in the Wannier function basis $|W^m_i\rangle$ (m is orbital index, i is site index), which is defined as the Fourier transform of a certain linear combination of Bloch functions $|\psi_{nk}\rangle$ (n is the band index and k is the wave vector in reciprocal space) can be written in the general form

$$t^{mm'}_{ij} = \langle W^m_i \Bigg| \left(\sum_{n,k} |\psi_{nk}\rangle \epsilon_n(k) \langle \psi_{nk}| \right) \Bigg| W^{m'}_j \rangle, \tag{2}$$

where $\epsilon_n(k)$ is the eigenvalue in the basis of linearized muffin-tin orbitals. The calculated inter-ring and intraring hopping parameters between $3d$ xy orbitals of vanadium atoms are presented in Table I. These values are in excellent agreement with the results of the downfolding procedure.[9] One can see that intraring hopping integrals are in the range −120 meV to −170 meV. The inter-ring hopping integrals between occupied xy orbitals of vanadium atoms are smaller than the intraring ones.

Having set up the picture of the dynamics of individual electrons we shall now introduce their on-site Coulomb interaction U to obtain the one-band Hubbard model

$$H_{Hub} = \sum_{i,j,\sigma} t_{ij} a^{+}_{i\sigma} a_{j\sigma} + \frac{U}{2} \sum_{i,\sigma} n_{i\sigma} n_{i-\sigma}, \tag{3}$$

where $n_{i\sigma}=a^{+}_{i\sigma}a_{i\sigma}$ is the particle-number operator. Based on the obtained hopping integrals, we have estimated the exchange interaction parameters using the expression $J^{xy}_{ij} = 4(t^{xy}_{ij})^2/U$ (see Table I), which appears upon mapping the one-band Hubbard model onto the Heisenberg model in the

TABLE I. Calculated hopping integrals between *xy* orbitals of vanadium atoms for the one-orbital model and estimated exchange interaction parameters $J_{ij}^{xy}[J_{ij}^{xy}=4(t_{ij}^{xy})^2/U, U=2.3\text{ eV}]$ of $Na_2V_3O_7$ (in meV).

i-j	t_{ij}^{xy}	J_{ij}^{xy}
(V1-1)-(V2-9)	−169	49.67
(V1-1)-(V3-16)	−145	36.56
(V1-1)-(V2-8)	−135	31.70
(V2-7)-(V3-18)	−138	33.12
(V2-9)-(V3-18)	−118	24.22
(V2-9)-(V3-15)	−36	2.25
(V1-1)-(V2-10)	−32	1.78
(V1-1)-(V3-15)	−6	0.06
(V1-2)-(V3-15)	−15	0.39

limit $U \gg t$, and which only describes the antiferromagnetic superexchange process due to the hybridization between nondegenerate orbitals. The sum in Eq. (2) runs over all bands. Therefore in the *xy*-orbital model we take into account all interaction paths between *xy* orbitals on different vanadium atoms.

In order to check the reliability of the mapping of the band structure onto the one orbital tight-binding model [Eq. (1)] we have also derived a five-orbital model described by a tight-binding Hamiltonian that includes five orbitals per V site,

$$H_{TB}^{full} = \sum_{\substack{i,j,\sigma \\ m,m'}} t_{ij}^{mm'} a_{im\sigma}^{+} a_{jm'\sigma} \tag{4}$$

using the projection procedure to calculate the hopping integrals. The results of this calculation are presented in Table II.

One can see that the hopping parameters between the occupied *xy* orbitals in the five-orbital model are not exactly the same as in the one-orbital model. This is due to the fact that the hybridization between filled and vacant orbitals is explicitly taken into account in the five-orbital model. It is also found that the sums of the squares of the hopping parameters between occupied and vacant orbitals I_{ij}^{f} are larger than those between filled orbitals, I_{ij}^{a}. Therefore one can expect that the Heisenberg model obtained from the one-band Hubbard model of Eq. (3) through perturbation theory is not sufficient in order to describe the magnetic couplings between vanadium atoms in $Na_2V_3O_7$.

TABLE II. Calculated hopping integrals between the 3*d* orbitals of vanadium atoms including five orbitals per V site model (in eV). t_{ij}^{mm} corresponds to the hopping process between the filled *xy* orbitals of *i*th and *j*th vanadium atoms, while $t_{ij}^{mm'}$ corresponds to the hopping parameters between filled and vacant orbitals.

i-j	t_{ij}^{mm}	$I_{ij}^{a}=(t_{ij}^{mm})^2$	$I_{ij}^{f}=\Sigma_{(m\neq m')}^{mm'}(t_{ij}^{mm'})^2$
(V1-1)-(V2-9)	−0.166	0.028	0.055
(V1-1)-(V3-16)	−0.153	0.023	0.043
(V1-1)-(V2-8)	−0.148	0.022	0.024
(V2-7)-(V3-18)	−0.155	0.024	0.043
(V2-9)-(V3-18)	−0.109	0.012	0.038
(V2-9)-(V3-15)	−0.042	0.002	0.036
(V1-1)-(V2-10)	−0.041	0.002	0.031
(V1-1)-(V3-15)	−0.001	0	0.069
(V1-2)-(V3-15)	−0.028	0.001	0.046

III. LDA+*U* CALCULATION

The main goal of the LDA+U method[16] is to take into account the Coulomb correlations of localized states, which are disregarded in LDA. The former method has proven to provide reasonable results for a number of strongly correlated systems.[16,17] The effective Coulomb interaction U and the effective intraatomic exchange J_H, which represent external parameters in a self-consistent cycle of the LDA+U scheme, are determined from the first-principle calculation by the constrained LDA method. This calculation scheme was described elsewhere.[18] The Coulomb interaction parameter U and intraatomic exchange J_H have been estimated as $U=2.3$ eV and $J_H=0.98$ eV. The Brillouin zone integration in our calculation has been performed in the grid generated by using (4,4,4) divisions.

Our LDA+U calculations show that the magnetic structure of $Na_2V_3O_7$ is frustrated with respect to magnetic couplings, i.e., we cannot find a collinear spin configuration which corresponds to the minimum of the total energy of the system. We have performed the LDA+U calculations for two magnetic configurations (Fig. 4). The results of these calculations are presented in Table III. One can see that in both magnetic configurations $Na_2V_3O_7$ is an insulator with an energy gap of 1 eV. The calculated average value of the magnetic moment of vanadium atoms is about $0.88\mu_B$, which is in good agreement with experimentally observed spin-1/2 moment.[19]

Following Lichtenstein *et al.*,[7] we determine the exchange interaction parameter between vanadium atoms via the second variation of the total energy with respect to small deviations of the magnetic moments from the collinear magnetic configuration. The exchange interaction parameters J_{ij} of the spin Hamiltonian $H=\Sigma_{i>j}J_{ij}\vec{S}_i\vec{S}_j$, where $S=1/2$, can be written in the following form:[7,20]

$$J_{ij} = \frac{2}{\pi}\int_{-\infty}^{E_F} d\epsilon \,\mathrm{Im} \sum_{\substack{m,m' \\ m'',m'''}} (\Delta_i^{mm'} G_{ij\downarrow}^{m'm''} \Delta_j^{m''m'''} G_{ji\uparrow}^{m'''m})$$

where the on-site potential $\Delta_i^{mm'}=H_{ii\uparrow}^{mm'}-H_{ii\downarrow}^{mm'}$ and the Green function is calculated in the following way:

$$G_{ij\sigma}^{mm'}(\epsilon) = \sum_{k,n} \frac{c_{i\sigma}^{mn*}(k)c_{j\sigma}^{m'n}(k)}{\epsilon - E_{\sigma}^{n}}. \tag{5}$$

Here $c_{i\sigma}^{mn}$ is a component of the nth eigenstate, and E_{σ}^{n} is the corresponding eigenvalue. In order to define the contributions to the total exchange interactions between vanadium

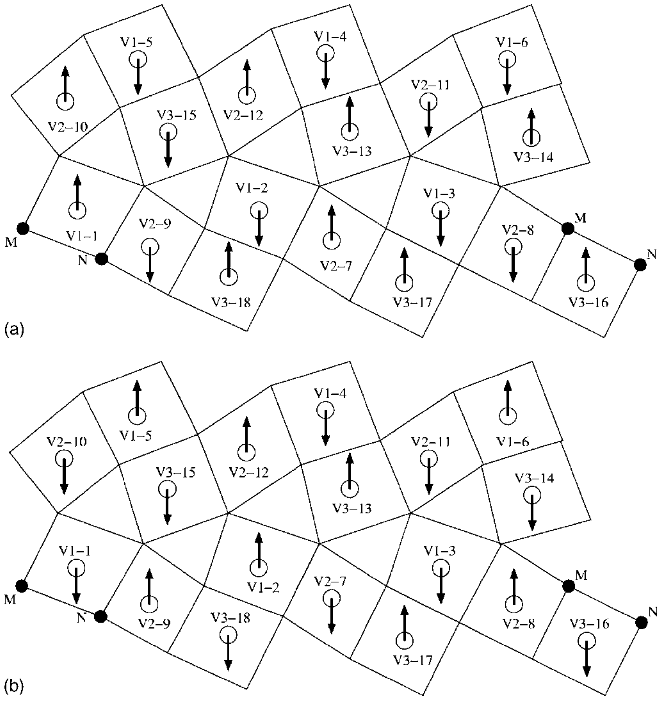

FIG. 4. The different magnetic configurations for $Na_2V_3O_7$ used in the LDA+U calculation. The arrows denote the directions of the magnetic moments, which lie along the z axis.

atoms from different pairs of $3d$ orbitals, we diagonalize the on-site potential in the following way: $\Delta_i^{mm'}=A_i^{mk}\tilde{\Delta}_i^{kk}(A_i^{km'})^*$, where $\tilde{\Delta}_i^{kk}$ is the on-site potential which is diagonal in orbital space and the matrix A defines the basis where Δ is diagonal. The exchange interaction between the kth orbital of site i and the k'th orbital of site j is given by

$$J_{ij}^{kk'}=\frac{2}{\pi}\int_{-\infty}^{E_F} d\epsilon \,\mathrm{Im}(\tilde{\Delta}_i^{kk}\tilde{G}_{ij\downarrow}^{kk'}\tilde{\Delta}_j^{k'k'}\tilde{G}_{ji\uparrow}^{k'k}),$$

where $\tilde{G}_{ij\sigma}^{kk'}=\Sigma_{mm'}A_i^{km}G_{ij\sigma}^{mm'}(A_j^{m'k'})^*$. In Eq. (5), the index n runs over all states. Therefore we take into account all interaction paths between the ith and jth atoms.

Our calculated values of the total exchange couplings are presented in Table IV. One can see that there is a qualitative *and* quantitative disagreement between the exchange interactions J_{ij}^{xy} deduced from the hopping parameters (Table I) and the total exchange interaction integrals J_{ij} obtained by the Green function method (Table IV). Therefore the simple model estimation $J_{ij}=4(t_{ij}^{xy})^2/U$ does not work in the case of $Na_2V_3O_7$. One has to take into account the low symmetry of this compound.

TABLE III. Results of LDA+U calculations for different types of magnetic configurations (see Fig. 4).

	Conf. 1	Conf. 2
Energy gap (eV)	1.14	1.18
Magnetic moment (μ_B)	0.87	0.89

TABLE IV. Calculated exchange interaction parameters of $Na_2V_3O_7$ (in meV). Negative couplings denote ferromagnetic exchange interactions. J_{ij}^{AF} is the contribution to the total exchange interaction coming from the coupling between filled orbitals of the ith and jth atoms, while J_{ij}^{FM} is the sum of the exchange interactions between filled and vacant orbitals of the ith and jth sites. The contributions to the total exchange interactions between vanadium atoms obtained by using extended Kugel-Khomskii model (see text below) are presented in parentheses.

i-j	J_{ij}	J_{ij}^{AF}	J_{ij}^{FM}
(V1-1)-(V2-9)	31.8	54.2 (48.7)	−22.4(−26.2)
(V1-1)-(V3-16)	13.4	35.4 (40)	−22.0(−20.5)
(V1-1)-(V2-8)	22.3	34.5 (38.2)	−12.2(−11.4)
(V2-7)-(V3-18)	15.5	35.6 (41.7)	−20.1(−20.5)
(V2-9)-(V3-18)	−5.8	16.3 (20.8)	−22.1(−18.1)
(V2-9)-(V3-15)	−12.2	∼0(3.4)	−12.2(−17.2)
(V1-1)-(V2-10)	−14.0	∼0(3.4)	−14.0(−14.7)
(V1-1)-(V3-15)	−36.9	0.4 (0)	−37.3(−32.8)
(V1-2)-(V3-15)	−27.7	0.6 (1.7)	−28.3(−21.9)

We have calculated the different contributions to the intraring and inter-ring exchange couplings. It was found that the antiferromagnetic exchange interaction between occupied orbitals J_{ij}^{AF} (Table IV) is in good agreement with J_{ij}^{xy} deduced from the hopping integrals (Table I). But there are also strong ferromagnetic contributions which are due to the hybridization between occupied (by electrons) and empty $3d$ orbitals of the vanadium atoms. For vanadium atoms which belong to different rings, one can see that the antiferromagnetic contribution due to the hybridization between occupied xy orbitals is approximately zero (Table IV). Thus, the main contribution to the total exchange interaction is given by hybridization between occupied and empty orbitals. A similar situation where the hybridization between filled and empty orbitals plays an important role was encountered for the layered vanadates CaV_2O_5, MgV_2O_5, CaV_3O_7, and CaV_4O_9.[3]

Let us first give an illustrative geometrical explanation of the obtained exchange interaction picture. In order to do so one can consider the simple two pyramid $S=1/2$ model presented in Fig. 5 with the assumption that the xy orbital of vanadium atom is occupied by one electron. The pyramid axes are collinear in the case of a perfect structure, therefore only the σ overlap between the V xy orbitals is nonzero. Thus the total exchange interaction is purely antiferromagnetic. The deviation from perfect geometry resulting from the rotation of a pyramid results in a decrease of σ-overlap between active orbitals and an increase of those between occupied and vacant orbitals. For instance, the overlap between the vacant $3z^2-r^2$ (right pyramid) and the filled xy orbital (left pyramid) results in an exchange interaction of ferromagnetic nature.

It might come as a surprise that two rather similar bonds such as (V1-1)-(V2-9) and (V2-9)-(V3-18) have very different interactions. In fact, a similar behavior was already found in other vanadium oxides (see, e.g., Refs. 3 and 21). To un-

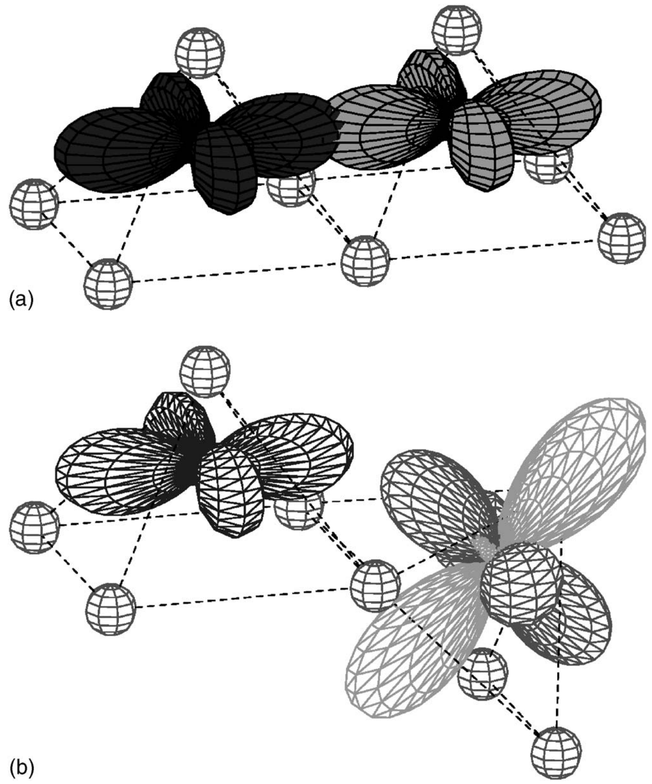

FIG. 5. Two pyramid *xy* model. The top and bottom figures correspond to perfect and distorted structures, respectively. The oxygen atoms are located at the edges of the pyramid.

TABLE V. Calculated crystal-field splittings between the occupied (xy) and the vacant orbitals ($yz,xz,3z^2-r^2,x^2-y^2$) of vanadium atoms obtained by using the projection procedure (in eV).

	Δ_{yz}	Δ_{xz}	$\Delta_{3z^2-r^2}$	$\Delta_{x^2-y^2}$
V1	1.10	1.71	3.05	2.55
V2	1.39	1.08	2.96	2.41
V3	1.18	1.60	2.95	2.27

derstand the origin of this difference, let us look in more details at these bonds. Both interactions (V1-1)-(V2-9) and (V2-9)-(V3-18) are the results of a strong competition between antiferromagnetic and ferromagnetic contributions. One can see that the values of ferromagnetic contributions, which are due to the hybridization between vacant and occupied orbitals, are similar (Table IV). It can be explained by the equality of the angles between the basal planes of the vanadium pyramids (see Fig. 5). On the other hand, the antiferromagnetic contribution to the total exchange interaction, which corresponds to the hybridization between occupied *xy* orbitals, is very sensitive to the V-V distance. Even a difference in distance as small as 0.157 Å results in a significant suppression of the hopping parameters (Table I and Table II) and correspondingly to a much smaller exchange interaction between occupied *xy* orbitals (Table IV) for the (V2-9)-(V3-18) bond in comparison with the (V1-1)-(V2-9) bond. Therefore the total exchange interactions for these bonds have different values as a consequence of the very distorted structure of that compound.

The resulting picture of magnetic interactions (Table IV) can be qualitatively explained within the Kugel-Khomskii model.[22] According to their investigation, for real materials it is necessary to consider all the 3*d* levels and the intraatomic exchange interaction J_H which leads to Hund's rule. We modify the Kugel-Khomskii model by introducing the splitting between the occupied orbital (denoted as 1) and other vacant orbitals,

$$H = \sum_{\substack{ij\sigma \\ mm' \\ (m\neq m')}} t_{ij}^{mm'} a^{+}_{im\sigma} a_{jm'\sigma} + \sum_{\substack{i\sigma\sigma' \\ mm'}} \frac{U_{mm'}}{2} n_{im\sigma} n_{im'\sigma'} \times (1-\delta_{mm'}\delta_{\sigma\sigma'}) + \sum_{im'\sigma} (1-\delta_{1m'})(\varepsilon_0+\Delta_{m'}) n_{im'\sigma} - \sum_{\substack{i\sigma\sigma' \\ mm'}} \frac{J_H^{mm'}}{2} (1-\delta_{mm'}) \times (a^{+}_{im\sigma} a_{im\sigma'} a^{+}_{im'\sigma'} a_{im'\sigma} + a^{+}_{im\sigma} a_{im'\sigma} a^{+}_{im\sigma'} a_{im'\sigma'}), \tag{6}$$

where ε_0 is the energy of the filled orbital and $(\varepsilon_0+\Delta_{m'})$ is the energy of the m'th vacant orbital. For simplicity we assume that $\varepsilon_0=0$ and we neglect the fact that different empty orbitals have different splittings, i.e., we assume that $\Delta_{m'}=\Delta$ (for vacant orbitals). It is also assumed that the Coulomb repulsion and the intraatomic exchange interaction do not depend on the particular orbital, i.e., $U_{mm}=U_{mm'}=U$ and $J_H^{mm'}=J_H$. The total exchange interaction can be expressed in terms of the sum of squares of the hopping integrals I_{ij}^{a} and I_{ij}^{f} presented in Table II, the splittings between filled and empty orbitals of vanadium atoms Δ, the on-site Coulomb U, and the intraatomic exchange interactions J_H in the following form:

$$J_{ij} = J_{ij}^{AF} + J_{ij}^{FM} = \frac{4I_{ij}^{a}}{U} - \frac{4I_{ij}^{f} J_H}{(U+\Delta)(U+\Delta-J_H)}. \tag{7}$$

The first term describes the antiferromagnetic coupling due to hybridization between active orbitals (occupied by electrons) at the *i*th and *j*th sites. The second term is the sum of the exchange interactions between vacant and filled orbitals. It is of ferromagnetic nature.

The values of the crystal-field splittings of different types of vanadium atoms obtained by using the projection procedure are presented in Table V. If we take for the the splitting Δ the average value of the crystal field splittings, namely 2 eV, the ferromagnetic contributions to the total exchange interactions estimated within the extended Kugel-Khomskii model are about two times smaller than those obtained using the Green function method (presented in Table IV). A physically more appealing approximation is to use in the model calculation the smallest value of the crystal field splitting, which corresponds to the first excitation energy for an electron between occupied and vacant orbitals. In our case this splitting is about 1.1 eV. The calculated contributions to the total exchange interactions between vanadium atoms for $\Delta = 1.1$ eV are presented in Table IV. One can see that we can qualitatively reproduce the antiferromagnetic and ferromagnetic contributions to the total exchange interactions between vanadium atoms using this simple model except for bond (V2-9)-(V3-18). In order to obtain full qualitative agreement with the Green function method results one should use $\Delta = 0.8$ eV, which is slightly less than the crystal-field splitting calculated by the projection procedure.

IV. CONCLUSION

We have investigated the electronic structure and the microscopic origin of the exchange interactions of $Na_2V_3O_7$. Based on our LDA+U results we predict that the value of the energy gap in electronic excitation spectra in this system is about 1 eV. The different contributions to the exchange interaction parameters have been calculated using the first-principle Green function method proposed by Lichtenstein. On the basis of the obtained results we argue that it is *not* correct to assume that the exchange interaction which is due to hybridization between active orbitals is a good approximation to the total exchange interaction between vanadium atoms for $Na_2V_3O_7$.

According to the present results, the main interactions are antiferromagnetic along the ring, ferromagnetic between the rings, and of the same order of magnitude. The presence of ferromagnetic bonds is consistent with the recent analysis of specific heat data reported in Ref. 23. The resulting Heisenberg model is strongly frustrated, with no obvious starting point for perturbation theory, hence no simple way to predict its properties. Such an analysis is left for future investigation.

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